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Date: 12 Dec 2006

To: Ms. Shiming Wu	**From:** Michael Bernshteyn
Application/Control Number: 10/500,082	**Art Unit:** 1713
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☐ **Urgent** ☐ **For Review** ☐ **For Comment** ☐ **For Reply** ☒ **Per Your Request**

Comments:
Dear Ms. Wu,
Per your request I fax you the copy of machine translation of two references used in my prior Office action: JP 09-324096 and JP 10-060207.
Thank you
Michael Bernshetyn

Number of pages 17 **including this page**

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-324096

(43)Date of publication of application : 16.12.1997

(51)Int.Cl. C08L 29/04
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(21)Application number : 08-166873

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(71)Applicant : DAI ICHI KOGYO SEIYAKU CO LTD

(72)Inventor : NISHIGUCHI HIROSHI
KITADA AKIRA

(54) WATER-SOLUBLE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a water-soluble film which is excellent in low-temp. solubility, does not exhibit any changes in physical properties with changes in temp. and humidity, and does not undergo the degradation in quality even when kept in contact with chemicals such as an alkali by compounding a specific modified PVA resin and a specific PVA resin.

SOLUTION: This compsn. comprises a modified PVA resin having anionic groups (pref. carboxyl and/or sulfo groups) pref. in an amt. of 2.0-40mol% (in terms of degree of modification) and a degree of polymn. of pref. 200-8,000 and a PVA resin having a degree of saponification of 70-99mol% and a degree of polymn. of pref. 200-8,000. The modified PVA resin having carboxyl groups is produced by subjecting PVA to the Michael addition reaction with acrylonitrile or acrylamide and partly or fully hydrolyzing the reaction product, and the one having sulfo groups is produced by subjecting PVA to the Michael addition reaction with vinylsulfonic acid, etc. The wt. ratio of the modified PVA resin to the PVA resin is pref. (95:5)-(5:95).

LEGAL STATUS

[Date of request for examination]

* NOTICES *

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] (A) The water soluble film which comes to contain the denaturation polyvinyl alcohol which has an anionic radical, and the (B) saponification degree 70 - 99-mol % of polyvinyl alcohol.
[Claim 2] The water soluble film according to claim 1 characterized by being denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely after said denaturation polyvinyl alcohol carries out Michael addition of the vinyl compound at polyvinyl alcohol.
[Claim 3] The water soluble film according to claim 1 characterized by being denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely after said denaturation polyvinyl alcohol carries out Michael addition of acrylonitrile or the acrylamide at polyvinyl alcohol.
[Claim 4] Water-soluble wrapping which consists of a water soluble film according to claim 1 to 3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the water-soluble wrapping which consists of the polyvinyl alcohol system film and this film of a cold-water fast-melting mold in detail about a cold-water fast-melting mold water soluble film and water-soluble wrapping.
[0002]
[Description of the Prior Art] The package of a water soluble film, a cleaning agent, etc. is broadly used as wrapping which presents water solubility from polyvinyl alcohol (it being called Following PVA) being able to carry out [film]-izing comparatively easily, and excelling before also in reinforcement.
[0003] Generally as PVA used for these, 80 - 90% saponification object which presents dissolved water in fuel, especially low-temperature-hot-water solubility (low-temperature fusibility) is used.
[0004]
[Problem(s) to be Solved by the Invention] However, in the conventional PVA film, even if it is using PVA of the above-mentioned partial saponification object as the raw material, the engine performance satisfied not necessarily is not obtained in the application which the solubility in low temperature may be inadequate for, therefore is asked for fastmelt [in low temperature].
[0005] Moreover, since a saponification reaction advanced by generating of film breakage, such as a crack, or contact to an alkaline substance under low temperature and low humidity, cold-water solubility fell further and there was a problem that it could not be used for a package of an alkaline substance.
[0006] Furthermore, since an insoluble ghost may generate these PVA(s) film by being exposed to an elevated temperature at the time of heat sealing, in the agricultural-chemicals package, the problem that nozzle plugging occurs at the time of agricultural-chemicals use with a sprayer is pointed out.
[0007] On the other hand, the applicant has proposed previously the water soluble film using the denaturation polyvinyl alcohol (henceforth "Denaturation PVA") which introduced the anionic radical into PVA (Japanese Patent Application No. No. 179064 [seven to]), and this is very excellent in cold-water fastmelt, and deterioration by alkali and the film breakage under low temperature and low humidity can also be prevented. However, if the rate of denaturation is gathered in order to improve cold-water fastmelt, since the hygroscopicity of a film will become large, there is a problem that humidity must be controlled, in the film of this denaturation PVA, and manufacture of wrapping.
[0008] The purpose of this invention is excellent in the PVA system water soluble film which solved the above-mentioned problem, i.e., cold melting nature, and to temperature and humidity, its physical-properties change is small, and it does not have deterioration in a package of an alkaline substance, and suppresses generating of a non-melt to the minimum, and is to offer the PVA system water soluble film which holds the reinforcement as wrapping.
[0009]
[Means for Solving the Problem] this invention persons blend wholeheartedly the denaturation PVA which has an anionic radical, and PVA which has the saponification degree of the specific range at a fixed rate in view of the above-mentioned trouble as a result of examination. It had fastmelt [to the cold

water easily exceeding anticipation when the obtained film is only mixed], and also to temperature and humidity, change of physical properties was small and it resulted solving problems, such as film breakage under low temperature and low humidity, and insolubilization by alkali, in header this invention. That is, it is the water soluble film which comes to contain the denaturation polyvinyl alcohol which has (A) anionic radical, and the (B) saponification degree 70 - 99-mol % of polyvinyl alcohol.
[0010]
[Embodiment of the Invention] The denaturation PVA which has anionic [which is the (A) component of this invention first] is explained in full detail below.
[0011] Although there is especially no limitation in the polymerization degree of the anion denaturation PVA used by this invention, 200-8,000 are good and 300-4,000 are preferably good. If polymerization degree is less than 200, sufficient film reinforcement will not be obtained, and there is a problem that hygroscopicity becomes large. On the other hand, when polymerization degree exceeds 8,000, since water-solution viscosity is high, not only fastmelt [to cold water] falls, but it cannot dissolve in high concentration but there is a problem that productivity falls.
[0012] As a rate of denaturation of an anionic radical, 2.0-40-mol % is good, and it is preferably [4.0-30 mol% of] good. If it is less than [2.0 mol %], while fastmelt [to cold water] will fall, there is a possibility of causing the film breakage under low temperature and low humidity. The thing exceeding 40-mol % on the other hand is difficult to manufacture.
[0013] Although a carboxyl group, a sulfone radical, a phosphate group, etc. are mentioned as a class of anionic radical, a carboxyl group and a sulfone radical are desirable in respect of economical efficiency and the ease of carrying out of manufacture.
[0014] As carboxyl group denaturation PVA used for this invention, after copolymerizing vinyl acetate, an itaconic acid, or a maleic acid, the so-called post-denaturation PVA which introduces a direct carboxyl group into the so-called copolymerization denaturation PVA by which it is saponified and obtained, or PVA is mentioned, for example.
[0015] There are an approach of carrying out the Michael addition reaction of the approach of carrying out piece esterification of the PVA by a maleic anhydride etc., the method of carrying out the substitution reaction of the monochloroacetic acid etc. to PVA, the acrylic acid, etc. to PVA as an approach of introducing a carboxyl group into PVA by post-denaturation, the approach of making it hydrolyze partially or completely, after carrying out the Michael addition reaction of acrylonitrile, the acrylamide, etc. similarly, etc. Among these, conversion is high and the approach of hydrolyzing in that the thing of the rate of high denaturation is obtained, after carrying out Michael addition of acrylonitrile or the acrylamide is desirable.
[0016] On the other hand, as an approach of introducing a sulfone radical into PVA, there is a method of making PVA carry out Michael addition of the approach and vinyl sulfonic acid which are saponified after copolymerizing vinyl acetate, a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound sulfonic acid, a meta-allyl compound sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid (it is called Following AMPS), etc. or its salt, AMPS, or its salt etc., for example. Among these, conversion is high and the method of making PVA carry out Michael addition of AMPS or its salt in that the thing of high denaturation is obtained is desirable.
[0017] Na salt, K salt, etc. are mentioned as a salt of Above AMPS.
[0018] Two or more sorts of degeneration methods may be used [in / with a natural thing / manufacture of the anion denaturation PVA] together in the above-mentioned anion-ized agent list.
[0019] Next, PVA of the (B) component is explained in full detail. The saponification degree of PVA which is the (B) component used for this invention is 70 - 99-mol %, and is 80 - 95-mol.% preferably.
[0020] When a saponification degree is less than [70 mol %], while cold-water fastmelt falls, the engine performance is not satisfied in respect of alkali resistance. On the other hand, when exceeding 99-mol %, it is easy to generate the film crack a cold-water fastmelt fall (cold-water insolubilization) and under low temperature and low humidity.
[0021] 200-8,000 are good at the reason same about polymerization degree as the aforementioned (A) component, and 300-4,000 are preferably good.

[0022] (A) the mixing ratio of a component and the (B) component -- a rate can be chosen as arbitration by (A):(B) =95-5:5-95% of the weight of within the limits. There is especially no limit in a mixed approach, and if it is a solid thing, it mixes with fine particles, or each can be used as a water solution and it can also mix.
[0023] Thus, although a process is not restricted especially about film-ization of the obtained PVA system constituent, the same process as a well-known PVA film can be conventionally applied correspondingly.
[0024] For example, after preparing the water solution of these PVA(s) system constituent, the cast is carried out to plastic film, such as a belt and PET, and a release paper, or drum lifting, and the casting method to dry is common.
[0025] Although the thickness of the film of this invention can be set as arbitration according to the purpose of use, the thickness of the film finally obtained also in which film-ized approach has good 10-100 micrometers in respect of mechanical strength and water fastmelt, and its 10-70 micrometers are more suitably good.
[0026] Furthermore, since the film of this invention gives flexibility, a plasticizer can be used for it if needed. As a plasticizer used for these, the plasticizer used for the usual PVA film can be used, and ethylene glycol, a glycerol, diglycerol, and a low-molecular-weight polyethylene glycol (molecular weight: 600 or less) are especially good. Moreover, a coloring agent, a release agent, etc. can be blended or applied within limits which do not spoil the main point of this invention. Furthermore, concavo-convex processing of embossing etc. may be performed in that blocking prevention processing and a fine sight are raised on a film.
[0027] The water-soluble PVA system film of this invention obtained as mentioned above is a material with which have fastmelt [excellent in cold water], an alkaline substance etc. does not deteriorate in a package of a chemical, but it has a material and the reinforcement as wrapping further. Therefore, it has the engine performance which was very excellent as wrapping, such as agricultural chemicals.
[0028] The cold-water fastmelt as used in the field of this invention means the high-speed solubility of the film which water temperature shows in 10 degrees C or less. Although the film of this invention is suitable also as the water imprint film which is the application of the water soluble film currently used conventionally, or various unit wrapping, it is possible to use it for the wrapping to which use was restricted especially conventionally and which requires fastmelt [in low water temperature].
[0029]
[Example] Hereafter, an example explains this invention to a detail further. In addition, among a sentence, as long as there is no notice especially about the section or %, and a certain thing, they are weight criteria.
[0030] (A) The example of the example manufacture of manufacture 1 vinyl-acetate 75 section of a component, the methanol 500 section, the itaconic-acid 4.85 section, the NaOH1.10 section, and the azobisisobutyronitril 0.3 section were taught to the separable flask, and the polymerization was carried out at 70 degrees C for 9 hours. The conversion at this time was 81%. After removing unreacted vinyl acetate, 1/10 of NaOH(s) of the amount of theory were added, and it saponified at 40 degrees C for 5 hours. The polymerization degree of the acquired carboxy denaturation PVA was 1,200 and saponification degree % of 96.3 mols. Moreover, when analyzed by NMR, the rate of carboxyl denaturation was 3.3-mol %.
[0031] The PVA(polymerization-degree 500 and saponification degree % of 88.2 mols)490 section, the NaOH200 section, the 50%-monochloroacetic acid water-solution 420 section, and the isopropyl alcohol 200 section were added to the broadside blender of example of manufacture 24 liter capacity, and it stirred at 60 degrees C for 8 hours. When it dried after the methanol refined the obtained product, and analyzed by colloidal titration, the rate of carboxy denaturation was 16.2-mol %.
[0032] The PVA(polymerization-degree 2,500 and saponification degree % of 98.8 mols)440 section, the 30%-NaOH water-solution 200 section, and the 50%-acrylamide water-solution 484 section were added to the broadside blender of example of manufacture 34 liter capacity, and it stirred at 60 degrees C for 8 hours. Subsequently, the 50%-NaOH100 section was added and hydrolysis was performed at 90

degrees C for 1 hour. When the obtained powder was analyzed by NMR, the rate of carboxyl denaturation was 29.3-mol %.

[0033] Instead of the 450%-acrylamide water-solution 484 of examples of manufacture section, it carried out by the same approach as the example 3 of manufacture except [all] having used the acrylonitrile 250 section. When the obtained powder was analyzed by NMR, the rate of carboxyl denaturation was 37.6-mol %.

[0034] The PVA(polymerization-degree 1,700 and saponification degree % of 98.5 mols)440 section, the 50%-NaOH water-solution 280 section, and the 50%-AMPS water-solution 828 section were added to the broadside blender of example of manufacture 54 liter capacity, and it stirred at 80 degrees C for 7 hours. When the obtained powder was analyzed by NMR, the rate of sulfone radical denaturation was 14.3-mol %.

[0035] The PVA(polymerization-degree 5,000 and saponification degree % of 98.2 mols)440 section, the 30%-NaOH water-solution 70 section, and the 50%-acrylamide water-solution 284 section were added to the broadside blender of example of manufacture 64 liter capacity, and it stirred at 60 degrees C for 4 hours. Subsequently, the 50%-NaOH125 section was added and hydrolysis was performed at 70 degrees C for 1 hour.

[0036] Subsequently, the 50%-AMPS sodium salt water-solution 460 section was added, and it stirred at 80 degrees C for 4 hours. When the obtained powder was analyzed by NMR, the rate of 17.3-mol % and sulfone radical denaturation of the rate of carboxyl denaturation was 6.5-mol %.

[0037] It blended at a rate which showed examples 1-6, and the example 1-2 (A) component of a comparison and the (B) component in Table 1, and eight sorts of films for a trial were prepared by the following approach.

[0038]

[Table 1]

	(A) 成分	固形分割合	(B) 成分	固形分割合
実施例 1	製造例1の変性PVA	35部	重合度2500, けん化度 71.1モル%のPVA	65部
実施例 2	製造例2の変性PVA	60部	重合度1700, けん化度 94.3モル%のPVA	40部
実施例 3	製造例3の変性PVA	70部	重合度1700, けん化度 88.5モル%のPVA	30部
実施例 4	製造例4の変性PVA	50部	重合度4000, けん化度 81.7モル%のPVA	50部
実施例 5	製造例5の変性PVA	95部	重合度 500, けん化度 85.1モル%のPVA	5部
実施例 6	製造例6の変性PVA	5部	重合度1700, けん化度 90.2モル%のPVA	95部
比較例 1	製造例3の変性PVA	30部	重合度1700, けん化度 65.5モル%のPVA	70部
比較例 2	—	-	重合度1700, けん化度 94.3モル%のPVA	100部

[0039] It mixed at a rate of a request of preparation **** of a film, and the denaturation PVA of the (A) component and PVA of the (B) component, and to the obtained PVA system mixture and this PVA system mixture, 3% of glycerol was dissolved in 80-degree C water so that it might become the viscosity of 15000 - 25000 mPa-s (BH mold viscometer, 20rpm, 25 degrees C). After cooling to a room temperature, it cast on the PET film, and dried at 100 more degrees C after 24-hour neglect for 1 hour, and the film for a trial with a thickness of 40 micrometers was prepared. About the obtained film, the performance test was carried out by the following approach. The result was indicated to Table 2.

[0040] The dissolution rate trial film to water was cut to 1cmx1cm, the mark of + was put in the aquosity Magic, it prepared for the 1l. beaker 500 cc of 10-degree C water beforehand, the film was dropped all over the quiescence water surface, and time amount until the mark of + disappears completely was measured. In addition, when a film adhered to round-head relaxation and a beaker side face, it measured again. In addition, the result was performed by three averages and displayed in the unit (second). Furthermore, even the water temperature of 5 degrees C was evaluated completely like the

above. In addition, what is not dissolved in 300 seconds presupposed "It is insoluble."
[0041] A machine strength test film is held to 20-degree-C65%RH for 72 hours, and it is JIS. According to K7127, tensile strength (TB:kg/cm strength) and an elongation percentage (EB:%) are measured, and it is JIS. Tearing strength (TR:kg/cm) was measured according to K7128.
[0042] The generating test trial film of an insoluble ghost was cut to 5cmx5cm, and 200 degrees C was pressed for 1 minute with a heat press. Then, this film was dissolved in 300 cc tap water, filtration desiccation was carried out and insoluble matter was measured.
[0043] An alkali-proof test trial film is cut to 1cmx1cm, and it puts on a petri dish, and is Na2 CO3 from a film. It carries and is Na2 CO3 about the film concerned. It covered and the dissolution rate to the water described above after one-month neglect in 40-degree C oven was measured. In addition, what is not dissolved in 300 seconds presupposed that it is insoluble.
[0044] Weight change of a film was measured under 25 degrees C of hygroscopicity, and RH80% of conditions. A part for the balanced water at the time of the increment in weight being balancing was computed as moisture absorption, and the following criteria estimated.
moisture absorption: -- the time of <20% -- hygroscopic : -- smallness and the time of moisture absorption:20-30% -- the time of moisture absorption:>30% among hygroscopic: -- hygroscopic : -- size
[0045] The film left for 48 hours under 0 degree C of film breakage and RH20% of conditions was bent, and the existence of a film crack was evaluated.
[0046] The comprehensive evaluation performance test result was judged synthetically, and it evaluated in five steps.
(It is good) 5->4->3->2->1 (bad)
[0047]
[Table 2]

		水溶解速度／秒		機械強度			不溶化物の発生	耐アルカリ試験／10℃	吸湿性	フィルム破損	総合評価
		10℃	5℃	TB(kg/cm²)	EB(%)	TR(kg/cm)	(%)	(秒)			
実施例	1	43	53	343	100	33	0.1	48	小	無	4
	2	35	43	355	100	37	0.0	37	小	無	5
	3	22	30	340	100	33	0.0	20	小	無	5
	4	28	33	385	95	40	0.0	24	小	無	5
	5	16	21	280	140	29	0.0	17	小	無	4
	6	48	60	310	120	30	0.2	55	小	無	4
比較例	1	不溶	不溶	220	190	23	—	不溶	中	無	2
	2	不溶	不溶	420	80	41	—	不溶	小	有	1

[0048]
[Effect of the Invention] The PVA system film of this invention consists of PVA excellent in the anion denaturation PVA which has the outstanding cold-water fastmelt, alkali resistance, etc., mechanical strength, humidity stability, etc., and when it carries out homogeneity mixing and both are film-ized, the outstanding engine performance possesses it according to the synergistic effect. That is, the PVA system film of this invention dissolves promptly also to 1. cold water.
2. It is hard to deteriorate even if it contacts chemicals, such as alkali.
3. It is stable to temperature and humidity, and there is little physical-properties change. For example, the film crack under low temperature and low humidity (0 degree C, 20%) etc. can be prevented.
4. The mechanical strength as a film or wrapping is excellent.
It has the features of **.

[0049] Therefore, when it uses for the PVA system film agricultural-chemicals wrapping of this invention etc., while being able to prevent plugging of the nozzle of a sprayer, quality degradation of the wrapping in an environment with inferior temperature and humidity conditions according [or] to a chemical can be controlled.

[Translation done.]

MENU SEARCH INDEX DETAIL JAPANESE

1 / 1

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-060207

(43)Date of publication of application : 03.03.1998

(51)Int.Cl. C08L 29/04
C08J 5/18
C08K 3/00

(21)Application number : 08-221054

(22)Date of filing : 22.08.1996

(71)Applicant : DAI ICHI KOGYO SEIYAKU CO LTD

(72)Inventor : NISHIGUCHI HIROSHI
WATANABE TOSHIO
KITADA AKIRA

(54) WATER-SOLUBLE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject film suitable for a packaging material, etc., slight in change of physical properties to temperature/humidity, capable of suppressing greasiness followed by moisture absorption to the minimum and exceeding in low-temperature solubility, strength and handle, comprising a specific modified polyvinyl alcohol and prescribed fine powder.

SOLUTION: This water-soluble film comprises (A) a modified polyvinyl alcohol such as one obtained by subjecting a polyvinyl alcohol having 2.0-40.0mol% modification ratio by an anionic group such as carboxyl group to Michael addition with a vinyl compound such as acrylonitrile or acrylamide and partially or completely hydrolyzing the resulting substance and (B) preferably 2.0-20wt.% (based on the component A) of fine powder such as clay which has ≤150μm average particle diameter and is water-insoluble or slightly water- soluble. A water-soluble packing material is obtained from the water-soluble film.

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CLAIMS

[Claim(s)]
[Claim 1] (A) the denaturation polyvinyl alcohol and (B) mean particle diameter whose rate of denaturation by the anionic radical is 2.0-40.0-mol % -- water 150 micrometers or less -- the water soluble film which comes to contain insoluble or poorly soluble impalpable powder.
[Claim 2] The water soluble film according to claim 1 with which it is characterized by being denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely after said denaturation polyvinyl alcohol carries out Michael addition of the vinyl compound at polyvinyl alcohol.
[Claim 3] The water soluble film according to claim 1 with which it is characterized by being denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely after said denaturation polyvinyl alcohol carries out Michael addition of acrylonitrile or the acrylamide at polyvinyl alcohol.
[Claim 4] Water-soluble wrapping which becomes any 1 term of claims 1-3 from the water soluble film of a publication.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the water-soluble wrapping which consists of the polyvinyl alcohol system film and this film of the cold-water fast-melting mold which improved stickiness by moisture absorption in detail about a cold-water fast-melting mold water soluble film and water-soluble wrapping.
[0002]
[Description of the Prior Art] The package of a water soluble film, a cleaning agent, etc. is broadly used as wrapping which presents water solubility from polyvinyl alcohol (it being called Following PVA) being able to carry out [film]-izing comparatively easily, and excelling before also in reinforcement.
[0003] As PVA used for these, 80 - 90% saponification object which presents dissolved water in fuel, especially low-temperature-hot-water solubility (low-temperature fusibility) is common.
[0004]
[Problem(s) to be Solved by the Invention] However, in the conventional PVA film, even if it is using PVA of the above-mentioned partial saponification object as the raw material, the engine performance satisfied not necessarily is not obtained in the application which the solubility in low temperature may be inadequate for, therefore is asked for fastmelt [in low temperature].
[0005] Moreover, there were a problem that film breakage of a crack etc. occurs under low temperature and low humidity, and a problem that cold-water solubility fell further and it could not be used for a package of an alkaline substance since a saponification reaction advances by contact to an alkaline substance.
[0006] On the other hand, the applicant has proposed previously the water soluble film using the denaturation polyvinyl alcohol (henceforth "Denaturation PVA") which introduced the anionic radical into PVA (Japanese Patent Application No. No. 179064 [seven to]), and this is very excellent in cold-water fastmelt, and deterioration by alkali and the film breakage under low temperature and low humidity can also be prevented. However, if the rate of denaturation is gathered in order to improve cold-water fastmelt, since stickiness resulting from the hygroscopicity of a film will become large, there is a problem that humidity must be controlled, in the film of this denaturation PVA, and manufacture of wrapping.
[0007] The purpose of this invention is excellent in the PVA system water soluble film which solved the above-mentioned problem, i.e., cold melting nature, and to temperature and humidity, its physical-properties change is small, and it does not have deterioration in a package of an alkaline substance, and suppresses the stickiness accompanying moisture absorption to the minimum, and is to offer the PVA system water soluble film which holds the reinforcement as wrapping.
[0008]
[Means for Solving the Problem] The denaturation PVA whose rate of denaturation according [this invention persons] to an anionic radical the result of wholeheartedly examination in view of the above-mentioned trouble is 2.0-40.0-mol %, mean particle diameter -- water 150 micrometers or less -- the film

which comes to contain insoluble or poorly soluble impalpable powder It has fastmelt [to the cold water exceeding the water-soluble conventional PVA film]. Even if it not only solves the problem of insolubilization change of physical properties is small and according to the film breakage under low temperature and low humidity, and alkali, but absorbed moisture to temperature and humidity, it was not sticky, and it finds out that good aesthetic property is maintained and came to complete this invention.
[0009] namely, the denaturation polyvinyl alcohol and (B) mean particle diameter whose rate of denaturation according [the water soluble film of claim 1] to (A) anionic radical is 2.0 - 40.0-mol % -- water 150 micrometers or less -- it comes to contain insoluble or poorly soluble impalpable powder.
[0010] In the water soluble film of claim 1, the thing of claim 2 is denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely, after said denaturation polyvinyl alcohol carries out Michael addition of the vinyl compound at polyvinyl alcohol.
[0011] In the water soluble film of claim 1, the thing of claim 3 is denaturation polyvinyl alcohol obtained by hydrolyzing partially or completely, after said denaturation polyvinyl alcohol carries out Michael addition of acrylonitrile or the acrylamide at polyvinyl alcohol.
[0012] The water-soluble wrapping of claim 4 becomes any 1 term of claims 1-3 from the water soluble film of a publication.
[0013]
[Embodiment of the Invention] The denaturation PVA which has the anionic radical which is the (A) component which constitutes the water soluble film of this invention first is explained in full detail below.
[0014] (A) Although a carboxyl group, a sulfone radical, a phosphate group, etc. are mentioned as a class of anionic radical of the denaturation PVA of a component, a carboxyl group and a sulfone radical are desirable in respect of economical efficiency and the ease of carrying out of manufacture.
[0015] As carboxyl group denaturation PVA used for this invention, after copolymerizing vinyl acetate, an itaconic acid, or a maleic acid, the so-called copolymerization denaturation PVA saponified and acquired, the so-called post-denaturation PVA which introduces a direct carboxyl group into PVA and is acquired are mentioned, for example.
[0016] There are an approach of carrying out the Michael addition reaction of the approach of carrying out piece esterification of the PVA by a maleic anhydride etc., the method of carrying out the substitution reaction of the monochloroacetic acid etc. to PVA, the acrylic acid, etc. to PVA as an approach of introducing a carboxyl group into PVA by post-denaturation, the approach of making it hydrolyze partially or completely, after carrying out the Michael addition reaction of acrylonitrile, the acrylamide, etc. similarly, etc. Among these, conversion is high and the approach of hydrolyzing in that the thing of the rate of high denaturation is obtained, after carrying out Michael addition of acrylonitrile or the acrylamide is desirable.
[0017] On the other hand, as an approach of introducing a sulfone radical into PVA, there is a method of making PVA carry out Michael addition of the approach and vinyl sulfonic acid which are saponified after copolymerizing vinyl acetate, a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound sulfonic acid, a meta-allyl compound sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid (henceforth AMPS), etc. or its salt, AMPS, or its salt etc., for example. Among these, conversion is high and the method of making PVA carry out Michael addition of AMPS or its salt in that the thing of high denaturation is obtained is desirable.
[0018] Na salt, K salt, etc. are mentioned as a salt of Above AMPS.
[0019] Two or more sorts of degeneration methods may be used [in / with a natural thing / manufacture of the anion denaturation PVA] together in the above-mentioned anion-ized agent list.
[0020] 2.0-40.0-mol% of the rate of denaturation by the anionic radical is desirable, and is more desirable. [4.0-30-mol% of] While fastmelt [to cold water] falls that it is less than [2.0 mol %], there is a possibility of causing the film breakage under low temperature and low humidity. The thing exceeding 40.0-mol % on the other hand is difficult to manufacture.
[0021] Although especially the polymerization degree of the above-mentioned anion denaturation PVA used by this invention is not limited, 200-8,000 are desirable and 300-4,000 are more desirable.

Sufficient film reinforcement is not obtained with polymerization degree being less than 200. On the other hand, if polymerization degree exceeds 8,000, since water-solution viscosity becomes high, not only fastmelt [to cold water] falls, but it cannot dissolve in high concentration but the problem that productivity falls will arise.
[0022] next, the water of the (B) component -- insoluble or poorly soluble impalpable powder is explained in full detail.
[0023] the water used for this invention -- the mean particle diameter of insoluble or poorly soluble impalpable powder is 150 micrometers or less, and is 50 micrometers or less preferably.
[0024] If mean particle diameter exceeds 150 micrometers, the addition taken to prevent stickiness of a film will increase, consequently aesthetic property will be spoiled, and film reinforcement will also fall.
[0025] the water used for this invention -- as a class of insoluble or poorly soluble impalpable powder, clay, a kaolin, an aluminum hydroxide, a calcium carbonate, a titanium dioxide, a barium sulfate, a satin white, talc, a silicate, pulp, a cellulose, etc. are mentioned, and using independently if needed can also use together two or more sorts of these.
[0026] Although all of such impalpable powder prevent the stickiness accompanying moisture absorption and the effect on film physical properties is suppressed to the minimum, pulp, a cellulose, a calcium carbonate, clay, and a kaolin are excellent in especially this point.
[0027] As an addition of these impalpable powder, 0.5 - 40 % of the weight is desirable to the denaturation PVA of the (A) component, and 2.0 - 20% is more desirable. The stickiness prevention accompanying the moisture absorption which is the effectiveness of this invention as it is less than 0.5 % of the weight is not enough. On the other hand, if it exceeds 40 % of the weight, it will become difficult to acquire the film physical properties for which it was suitable as wrapping.
[0028] Thus, on the occasion of film-izing of the obtained denaturation PVA system constituent, especially a process is not restricted but can apply correspondingly the process of a well-known PVA film conventionally.
[0029] For example, after preparing the water solution (impalpable powder is carrying out suspension distribution) of these denaturation PVA system constituent, the cast is carried out to plastic film, such as PET, a release paper, a belt, or drum lifting, and the casting method to dry is common.
[0030] Although the thickness of the film of this invention can be set as arbitration according to the purpose of use, the thickness of the film finally obtained also in which film-ized approach has desirable 10-100 micrometers in respect of mechanical strength and water fastmelt, and its 10-70 micrometers are [thickness] more desirable.
[0031] Since flexibility is given, a plasticizer can be used for the film of this invention if needed. As a plasticizer used for these, the plasticizer used for the usual PVA film can be used, and ethylene glycol, a glycerol, diglycerol, and a low-molecular-weight polyethylene glycol (molecular weight: 600 or less) are especially good. Moreover, a coloring agent, a release agent, etc. can be blended or applied within limits which do not spoil the meaning of this invention. Furthermore, for the purpose of blocking prevention or improvement in a fine sight, concavo-convex processing of embossing etc. may be performed to a film.
[0032] The water-soluble PVA system film of this invention obtained as mentioned above is a material with which have fastmelt [excellent in cold water], do not deteriorate in the package of an alkaline substance etc., but it has a material and the reinforcement as wrapping further. Therefore, it has the engine performance which was very excellent as wrapping, such as agricultural chemicals.
[0033] In addition, the cold-water fastmelt as used in the field of this invention means the high-speed solubility of the film shown in the water temperature of 10 degrees C or less. Although the film of this invention is suitably used as the water imprint film which is the application of the water soluble film currently used conventionally, or various unit wrapping, it is also possible to use it as wrapping which had the limit in use in the further conventional water soluble film and which requires fastmelt [in low water temperature].
[0034]
[Example] Hereafter, an example explains this invention to a detail further. In addition, among a sentence, as long as there is no notice especially about the section or %, and a certain thing, they are

weight criteria.
[0035] 1.(A) The example of manufacture manufacture 1 vinyl-acetate 75 section of a component, the methanol 500 section, the itaconic-acid 4.85 section, the NaOH1.10 section, and the azobisisobutyronitril 0.3 section were taught to the separable flask, and the polymerization was carried out at 70 degrees C for 9 hours. The conversion at this time was 81%. After removing unreacted vinyl acetate, 1/10 of NaOH(s) of the amount of theory were added, and it saponified at 40 degrees C for 5 hours. The polymerization degree of the acquired carboxyl denaturation PVA was 1,200, and the saponification degree was 96.3-mol %. Moreover, when analyzed by NMR, the rate of carboxyl denaturation was 3.3-mol %.
[0036] The PVA(polymerization-degree 500 and saponification degree % of 88.2 mols)490 section, the 30%-NaOH200 section, the 50%-acrylamide water-solution 420 section, and the isopropyl alcohol 200 section were added to the broadside blender of example of manufacture 24 liter capacity, and it stirred at 60 degrees C for 8 hours. Subsequently, the 50%-NaOH50 section was added and hydrolysis was performed at 70 degrees C for 1 hour. It dried, after the methanol refined the obtained powder, and white powder was obtained. When this thing was analyzed by NMR, the rate of 12.2-mol % and amide denaturation of the rate of carboxyl denaturation was 8.9-mol %.
[0037] The PVA(polymerization-degree 2,500 and saponification degree % of 98.8 mols)440 section, the 30%-NaOH water-solution 200 section, and the 50%-acrylamide water-solution 484 section were added to the broadside blender of example of manufacture 34 liter capacity, and it stirred at 60 degrees C for 8 hours. Subsequently, the 50%-NaOH100 section was added and hydrolysis was performed at 90 degrees C for 1 hour. When the obtained powder was analyzed by NMR, the rate of carboxyl denaturation was 29.3-mol %.
[0038] Instead of the 450%-acrylamide water-solution 484 of examples of manufacture section, the same actuation as the example 3 of manufacture was performed except [all] having used the acrylonitrile 250 section. When the obtained powder was analyzed by NMR, the rate of carboxyl denaturation was 37.6-mol %.
[0039] The PVA(polymerization-degree 1,700 and saponification degree % of 98.5 mols)440 section, the 50%-NaOH water-solution 280 section, and the 50%-AMPS water-solution 828 section were added to the broadside blender of example of manufacture 54 liter capacity, and it stirred at 80 degrees C for 7 hours. When the obtained powder was analyzed by NMR, the rate of sulfone radical denaturation was 14.3-mol %.
[0040] The PVA(polymerization-degree 5,000 and saponification degree % of 98.2 mols)440 section, the 30%-NaOH water-solution 70 section, and the 50%-acrylamide water-solution 284 section were added to the broadside blender of example of manufacture 64 liter capacity, and it stirred at 60 degrees C for 4 hours. Subsequently, the 50%-NaOH125 section was added and hydrolysis was performed at 70 degrees C for 1 hour.
[0041] Subsequently, the 50%-AMPS sodium salt water-solution 460 section was added, and it stirred at 80 degrees C for 4 hours. When the obtained powder was analyzed by NMR, the rate of 17.3-mol % and sulfone radical denaturation of the rate of carboxyl denaturation was 6.5-mol %.
[0042] 2. It blended with the native PVA for the denaturation PVA ((A) component) of the preparation examples 1-6 of a film, the example 1 of a comparison, and the examples 1-6 of manufacture acquired by the 2 above, and a comparison at a rate which showed impalpable powder ((B) component) in Table 1, and eight sorts of films for a trial were prepared by the following approach.
[0043]
[Table 1]

	変性ＰＶＡの種類	（Ｂ）成分		
		種類	平均粒径	添加量[1]
実施例 1	製造例１の変性ＰＶＡ	パルプ	２１	５
実施例 2	製造例２の変性ＰＶＡ	カオリン	４３	１０
実施例 3	製造例３の変性ＰＶＡ	炭酸カルシウム	３	１０
実施例 4	製造例４の変性ＰＶＡ	炭酸カルシウム	１０	３５
実施例 5	製造例５の変性ＰＶＡ	クレー	１３	２０
実施例 6	製造例６の変性ＰＶＡ	セルロース	７	１５
比較例 1	製造例５の変性ＰＶＡ	－	－	－
比較例 2	未変性ＰＶＡ[2]	炭酸カルシウム	３	１０

1) 対変性ＰＶＡ重量％
2) 重合度1700，けん化度 88.2 モル％

[0044] First, after making water carry out suspension distribution of the impalpable powder of the (B) component, to the sum (a part for however, solid) of the denaturation PVA of a [preparation of film] (A) component, and the weight of these (A) (B) both components, 3% of glycerol was added and it dissolved. In addition, the solution viscosity at this time was adjusted so that it might become 15000 - 25000 mPa-s (BH mold viscometer, 20rpm, 25 degrees C). Subsequently, these were cast on the PET film, it dried at 100 more degrees C after 24-hour neglect for 1 hour, and the film for a trial with a thickness of 40 micrometers was prepared.
[0045] 3. about the evaluation profit **** film of a film, the performance test was carried out by the following approach. The result was indicated to Table 2.
[0046] The [dissolution rate to water] trial film was cut to 1cmx1cm, and the mark of + was put in the aquosity Magic. 500 cc of 10-degree C water was beforehand prepared for the 1l. beaker, said film was dropped all over the quiescence water surface, and time amount until the mark of + disappears completely was measured. When a film adhered to round-head relaxation and a beaker side face, it measured again. In addition, the result displayed 3 times of the averages in the "second." Furthermore, even the water temperature of 5 degrees C was evaluated completely like the above.
[0047] A [mechanical strength] trial film is held under the condition of 20 degrees C and 65%RH for 72 hours, and it is JIS. According to K7127, tensile strength (TB:kg/cm2) and an elongation percentage (EB:%) are measured, and it is JIS. Tearing strength (TR:kg/cm) was measured according to K7128.
[0048] A [alkali-proof test] trial film is cut to 1cmx1cm, and it puts on a petri dish, and is Na2 CO3 on a film. It carries and is Na2 CO3 about the film concerned. It covered and the dissolution rate to the water described above after one-month neglect in 40-degree C oven was measured. In addition, what is not dissolved in 300 seconds presupposed that it is insoluble.
[0049] [Tactile feeling (aesthetic property)] Tactile feeling after leaving a film under 25 degrees C and RH80% of conditions for 5 hours was judged in accordance with the criteria of the following [a feel].
[0050] O : -- Good **: -- sticky for a while x: -- stickiness bent the film left for 48 hours under large [film breakage] 0 degree C and RH20% of conditions, and evaluated the existence of a film crack.
[0051] The [comprehensive evaluation] above-mentioned performance test result was judged synthetically, and it evaluated in five steps.
[0052] (It is good) 5->4->3->2->1 (bad)
[Table 2]

		水溶解速度／秒		機械強度			耐アルカリ試験／10℃（秒）	触感	フィルム破損	総合評価
		10℃	5℃	TB(kg/cm²)	EB(%)	TR(kg/cm)				
実施例	1	40	59	339	100	34	45	○	無	4
	2	33	45	365	100	39	33	○	無	5
	3	25	33	346	100	39	24	○	無	5
	4	22	35	395	95	43	22	○	無	5
	5	15	23	290	140	27	12	○	無	4
	6	48	64	345	120	35	59	○	無	4
比較例	1	17	24	310	100	25	22	×	無	3
	2	140	110	390	90	46	不溶	○	有	1

[0053]
[Effect of the Invention] the anion denaturation PVA and mean particle diameter which have the cold-water fastmelt excellent in the PVA system film of this invention, alkali resistance, etc. -- water 150 micrometers or less -- the engine performance which came to contain insoluble or poorly soluble impalpable powder, and was excellent as a water soluble film is provided.
[0054] That is, the water soluble film of this invention according to claim 1 to 3 is stable to 3. temperature and humidity which cannot deteriorate easily even if it contacts chemicals, such as 2. alkali which dissolves promptly also to 1. cold water, and there is little physical-properties change. For example, even if it absorbs moisture under excellent in mechanical strength as 4. film [which can prevent the film crack under low temperature and low humidity (0 degree C, 20%) etc.], or wrapping 5. high humidity, it is not sticky, and it has the features -- good tactile feeling is maintained.
[0055] Therefore, the water-soluble wrapping of claim 4 which consists of a water soluble film of this invention can control quality degradation in an environment with inferior temperature and humidity conditions according [or] to a chemical while being able to prevent plugging of the nozzle of a sprayer, when each above-mentioned features are provided, for example, are used for agricultural-chemicals wrapping etc.

[Translation done.]